Comment on "Liquid-Liquid Phase Transition in Supercooled Yttria-Alumina"

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We welcome efforts made by Barnes *et al.* to study liquid-liquid transitions (LLT) in supercooled $Y_2O_{3x}-Al_2O_{3(100-x)}$ or AYx melts reported in a recent Letter [1]. The first order LLT in AY20, which we have identified *in situ* under equilibrium conditions [2,3] has a well-defined temperature T_{LL} at ambient pressure and a critical point at negative pressure. The LLT is also composition dependent, rising as x falls [3,4]. We identified this at 1788 K from (i) a peak in the small angle x-ray scattering (SAXS) intensity, (ii) a discontinuity in the structure factor $S(Q)$, and (iii) a "polyamorphic rotor" caused by periodic LLTs [Fig. 1(a)]—the flipping time and associated temperature spikes yielding the LLT density and entropy discontinuities in agreement with *ex situ* experiments [4]. Barnes *et al.* used similar experiments but could not reproduce (i) or (ii) in AY20 at 1788 K and attributed (iii) to 60 K instabilities sometimes encountered during sample conditioning [1]. We consider their null results for AY20 are due to (A) large neutron beam sizes in small angle neutron scattering (SANS), and (B) doubts in AYx composition. Moreover, comparison with our work [2] is obscured in [1] by reliance on apparent temperatures uncorrected for emissivity [5] and by inconsistent molar normalization leading to flaws in modelling LLTs from our data [3].

(A) In their SANS measurements [1] the mm radius droplet was overspilled by a 2 mm radius 4.5 Å beam. Because of the spherical liquid surface this results in total external reflection and cross fire contamination up to at least $2 \times 0.013 = 0.026$ Å^{-1}. Sub mm focused SAXS has none of these disadvantages [2] which is why it is sensitive to the rise and fall in scatter that occurs below 0.03 Å^{-1} [2] at the LLT (Fig. 1). Importantly, polyamorphic rotor action was recorded by L. Hennet during the SANS experiments with periodic 150 K spikes centered at 1940 K [Fig. 1(b)]. Polyamorphic rotors have large repetitive spikes thermally distinct from the oscillations illustrated in [1] which sometimes occur when molten drops contain inclusions.

(B) The sample preparation method of fusing 85 mg drops from weight-matched beads of separate oxides [6] is unreliable without validation of recovered samples. We fused mm radius drops by weighing material from 5 g powdered batches following repeated sintering and regrinding. Composition checks post experiment confirm $x <$ mol 1% accuracy. $S(Q)$'s of AYx melts at 2300 K are composition sensitive (Fig. 1). Measurements at 11-ID-C (APS) [2] and at ID11 (ESRF) [7] are in good agreement, with the positions of the first and second peaks Q_1 and Q_2, and size of the principal peak $S(Q_1)$ all scaling almost linearly with x, except for values fitted from the peak maxima at 2300 K from [1] Fig. 1. Rather than AY20, these triangulate with the composition AY14 ± 1. We already investigated AY15 until crystallization intervened at 1927 K [2] close to the rotor temperature shown in Fig. 1(b). If 1940 K marks the LLT for AY15 then, with our observation of 1788 K for AY20 [2], these results further demonstrate that for AYx liquids T_{LL} rises as x falls [3,4], and provide scope for future collaboration.

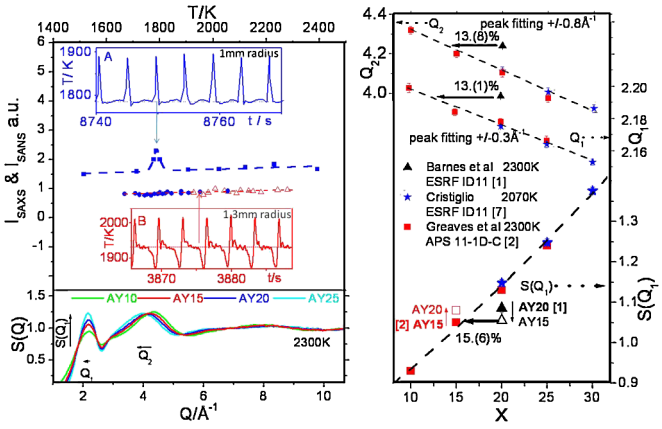

FIG. 1 (color online). Left. Upper: SAXS for AY20 ■ and AY15 Δ from [2] scaled to SANS for AY20 ● from [1], together with LLT rotor motion (A and B). Lower: $S(Q)$ for AYx liquids from [2] corrected for detector scattering angle thickness, with compositional changes marked. Right: trends in Q_2, Q_1 and $S(Q_1)$ with x. 2σ errors for Q_1 and Q_2 from peak-fitting and for $S(Q_1)$ from [1] within symbol size. Arrows between closed and open symbols ⇅ show shifts in $S(Q_1)$ for alternative compositions $x = 15 \leftrightarrow 20$. Horizontal arrows show $x = 14\% \pm 1\%$ as the likely composition for the Letter [1] rather than AY20.

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